Chapter 2

Special Cements

SPECIAL CEMENTS

1. DEFINITION

Special cements are cements with special properties that meet particular requirements which are not fulfilled by ordinary cements.

These properties refer either to the performance of cement in fresh and hardened concrete as well as in other cementitious blends, or to a special field of application. They can be produced with appropriate selection of clinker raw materials and/or cement constituents, adoption of special measures in manufacturing, tailored cement compositions.

As a consequence of these actions, special cements can still comply with existing standards on common cements, but very often they are better described in appropriate specifications, or otherwise they are produced on the basis of specific agreements between producer and user.

In spite of the several types listed in the following, their application is still limited in quantity and the total amount of marketed special cements can be estimated in the order of 10 to 15% of production. Nevertheless the additional possibilities given by the recently issued new cement standards and the increased severity of the environments where concrete is put into service are going to make this quantity increase in the near future.

2. TYPES OF SPECIAL CEMENTS

Special cements are usually developed and produced to meet performance and durability requirements, in particular

- improved strength development
- increased resistance to chemical attack
- improved compatibility with reactive aggregates
- suitability for use at elevated temperatures and pressures
- suitability for use in special applications
- applicability in architectural purposes

As already discussed in the chapter on special clinkers, special cements may belong to three main categories

- Portland cement or blended Portland cement
- Modified Portland cement
- non-Portland cement.

2.1 Special Portland Cements for Durability

Their main hydraulic constituent is generally Portland cement clinker, very often tailored to obtain special characteristics that yield the desired properties to the cement. For this reason, particular measures need to be taken in the production of clinker, expecially from the point of view of the selected raw materials to employ. In some cases this could not be enough or the involved costs are much higher than the obtained benefit.

So, the same or even better final properties can be achieved by blending clinker with appropriate mineral components and/or additions, as described in chapter , dealing with design and properties of blended cements.

Main durability characteristics for Portland type special cements are

- resistance to sulfate attack
- low heat of hydration
- resistance to pure water attack
- low alkali content or low reactivity with amorphous silica
- resistance to freeze-thaw cycles.

Before dealing with the different durability aspects that can require use of special cements, a general remark must be done. The main factor influencing durability is the proper design, production, compaction and curing of concrete. Any special cement, designed for the enhancement of durability will fail when used in the production of a poor concrete. A well compacted, high strength, low porosity concrete will be by far less prone to be attacked by external agents, even when produced with ordinary cements.

2.1.1 Sulfate resisting cements

Sulfates can be found in natural and industrial waters, as well as in soils. Soluble sulfates can react with lime and aluminates present in the hardened concrete and form respectively gypsum and ettringite. Both reactions entail expansion and consequent concrete deterioration. Sulfate resisting cements are characterized by a low C_3A content, to minimize the risk of ettringite formation. This type of binders set and harden normally and in fully compacted concrete are not attacked by sulfates in a wide range of concentration. At the same time they possess low-heat properties.

2.1.2 Low heat cements

Hydration reactions of cement develop heat. When cement is used in the production of mass concrete, temperature gradients generate between core and surface of the conglomerate cause strains and may eventually lead to cracking. Low heat cements have a reduced heat of hydration, obtained by altering the chemical composition (low C_3S and C_3A contents). The use of low-heat cement is recommended for mass concrete production or for large structural sections. They usually set and harden at a lower rate than for ordinary cements, especially in cold weather, but ultimate strengths may be higher. They possess also good sulfate resisting properties.

2.1.3 Leaching resistant cements

Waters with low salinity or a high content of carbon dioxide (CO2) are capable to dissolve hydration lime present in hardened concrete structures and may subsequently also subtract lime from silicate hydrates, thus causing damage to the hardened cement paste. Cements resisting to leaching have a low development of calcium hydroxide (lime) after hydration of clinker silicates, as a consequence of their low C_3S content. Their use is suggested in hydraulic works like basins, river barriers and sides. At the same time they possess rather low heat evolution characteristics.

2.1.4 Low alkali cements

Some aggregates may contain forms of reactive amorphous silica. In the presence of water this can react with the soluble alkali of cement and form locally an expansive gel that can deteriorate concrete. In such cases, *when the use of reactive aggregates is absolutely unavoidable,* the use of a cement proven to counteract alkali-silica reaction (ASR) is suggested. Such cements can either be low-alkali or blended cements, since the pozzolanic or slag material can immediately react with alkali and prevent subsequent reaction with aggregates in the hardened paste.

2.1.5 Sea-water resisting cements

Deterioration of concrete which is in contact to sea water takes place as a consequence of some of the already described phenomena. Concurring factors are chemical attack by $MgSO_4$, mechanical stress caused by tydal waves, crystallisation pressure due to deposition of salts in the wind and water line. Cold climates add freeze-thaw effects, while in warm areas some reactions are accelerated. Sea-water resisting cements are standardised in some countries, being moderate C_3A content or blended cements.

2.1.6 Freeze-thaw resisting cements

In harsh climates with high temperature differences and repeated freeze-thaw cycles, freezing of water contained in gel and aggregate pores will cause a volume increase of ab. 10% and the consequent development of internal pressure; repeated actions of this type deteriorate the concrete. Entrainment of air in form of microbubbles will produce a closed artificial porosity acting as expansion chambers for the ice generated. Some standards such as ASTM provide for cement types with air entrainment.

2.2 Blended Cements for Durability

In the chapters 2.1.1.to 2.1.5 specifications set limits for clinker components, i.e. maximum C_3A and C_3S content, maximum Na_20 equivalent, as reflected in the **ASTM C150** specification for Portland cement.

But in all of these cases, the simple "dilution" of clinker with a suitable pozzolan or a slag, when not simply the addition of limestone, will yield the same effect in terms of reduction of the content of the sensitive clinker component.

Additionally, the use of a mineral component like slag, pozzolan or fly ash will improve the durability and the pore structure of hardened concrete by lowering its lime content and porosity as a consequence of the enhanced development of calcium silicate hydrates.

Then, the ASTM **C595** and **C1157** deal with blended cements and set limits referred to the performance of cement with respect of sulfate resistance and heat of hydration, without any prescription on the basis of cement composition.

If we look at these durability aspects in the context of the European standard **ENV 197-1**, we can immediately realize that most of the Portland composite cements of the **II/B** type, with addition of 21 up to 35% of non-clinker materials, as well as type **III** (slag), type **IV**

(pozzolan) and type **V** (composite) cements can be considered as "special" with respect to many properties mainly related to durability.

Nevertheless, a CEN working group is now drafting new ENV 197 parts specifically dealing with special cements, in particular low heat- and sulfate resisting cements.

2.3 High Early Strength Cement, Rapid Hardening Cement

High early strength cement (HES) and rapid hardening cement (RHC) may either be finer than ordinary cement or have a special clinker composition.

Especially in the past, production of HES/RHC cements often required the production of a special clinker, with high C_3S and C_3A contents.

In present times, the improvements gained in grinding technology and in the use of *quality enhancers* as grinding aids, combined with the need of rationalization for storage and transports in cement plants, allow for the production of high early strength cements based on the same clinker used for ordinary binders. The higher grinding fineness and the related enhanced reactivity usually require increased gypsum dosage.

Physical properties of HES/RHC cements in comparison with ordinary Portland cements are shown in table 1. It should be noted that an increase in fineness would often also reflect in higher late strengths.

Table 1 Physical Properties of High Early Strength and Ordinary Portland Cement

Type	Blaine (cm^2/g)	Initial setting time (minutes)	Compr. strength MPa (ISO) 2 days	28 days
OPC	3000 ÷ 3500	150 ÷ 240	10 ÷ 20	38 ÷ 43
High early strength	3800 ÷ 4500	120 ÷ 180	20 ÷ 30	48 ÷ 55
Rapid hardening	4800 ÷ 5500	90 ÷ 150	30 ÷ 40	58 ÷ 67

The use of HES/RHC cements is indicated when a rapid strength development is required, e.g. if formwork has to be removed or re-used after a short time (precast elements production) or when sufficient strength is required for further construction (slipforming).

However, since rapid strength gain is usually associated to high rate of heat devlopment, HES/RHC cements should not be used in mass concrete or in large structural sections. On the other hand, concreting at low temperatures would profit from the use of a high heat cement as a safeguard against early frost damage.

2.4 Fast Setting Cement (Vicat Cement)

A particular type of fast setting cement is the so called Vicat cement from the name of its inventor and main producer. It is obtained by burning at low temperature (1200 to 1250 °C) selected natural marls with rather high alumina contents. The clinker produced is mainly composed of belite and aluminates; after grinding it is capable to set in a few minutes, developing sufficient strength to fulfil requirements for easy and fast repair or small construction jobs.

"Artificial" fast setting cement can be produced by blending OPC and High Alumina cement (see § 2.12) approximately at a 9:1 ratio.

2.5 Sulfo-aluminate Cement

Cements having calcium sulfo-aluminate ($C_4A_3S^*$) as main component. Examples of this binder type are type K cement produced in USA and the so called third cement series (TCS) in India and China. Typical composition ranges are reported in Table 4.

Characteristics of these cements are

* reduced setting times
* high workability, low water demand
* rapid strength development
* low shrinkage (even expansive)

Hydration of $C_4A_3S^*$ leads to the formation of ettringite, which is mainly responsible for early strength development. Microstructure of ettringite depends on the presence of lime. When ettringite forms in presence of lime it provokes expansion and this property is used to produce no-shrinkage cements. In the absence of lime, ettringite is not expansive and mainly contributes to strength development.

Binders of this type can then be used, according to mineralogy, to prevent shrinkage in concrete or to develop high early strength for special applications.

The blend of TCS cements with OPC yields to flash setting.

Table 4 Chemical and mineralogical composition of Sulfo-aluminate Cements

	Sulfo-aluminate clinker (type K)	**TCS sulfo-aluminate cement (SAC)**	**TCS ferro-aluminate cement (FAC)**
SiO_2	2 - 4	3 - 10	6 - 12
Al_2O_3	45 - 49	28 - 40	25 - 30
Fe_2O_3	1 - 2	1 - 3	5 - 12
CaO	37 - 39	36 - 43	43 - 46
SO_3	7 - 10	8 - 15	5 - 10
CaO free	0 - 0.3	0 - 0.3	0 - 0.3
mineralogical composition			
$C_4A_3S^*$	55 - 70	55 - 75	35 - 55
CA	15 - 20	-	-
C_2AS	15 - 20	-	-
C_4AF	0 - 5	3 - 6	15 - 30
C_2S	-	15 - 30	15 - 35

2.6 Regulated Set (Regset) Cement

Modified Portland cement type with rapid setting and hardening characteristics. The active component is a calcium fluoroaluminate (11 CaO. $7Al_2O_3$. CaF_2).

The regset cement is characterized by a setting time of 15 to 60 minutes. The setting is controlled by the addition of retarders (citric acid). Additional characteristic property is its unusually high early strength. A comparison between strengths achieved with Regset and HES cement is reported in Table 2.

Table 2 Properties of Regset and High Early Strength Cement

EN method	Regset Cement	H.E.S. Cement
Compr. Strength MPa		
2 hours	6	0
8 hours	8	2
16 hours	9	15
2 days	10	35
7 days	18	47
28 days	35	60
Setting time minutes		
Initial	45	120
Final	75	180

The very early strength gain makes this cement useful for all applications where there is a vital need for short times between placing and hardening of concrete, i.e. shotcrete, repairs on airport runways or highways, pavements.

Regset cements are batched, handled and mixed in pretty well the same way as Portland cements, making however the necessary provisions for rapid handling and placing of concrete. Although production is as cheap and easy as for Portland cement, the fast and often unpredictable setting behaviour puts serious limits to the use in constructions and the total world production is estimated in the order of 10000 tons/year.

2.7 Oil-well cements

Oil-well cements are developed for use in oil and gas wells and are designed to set and cure at high temperatures and pressures in well grouting. They can also be used for sealing water wells, waste disposal wells and geothermal wells. Cement plays an important part in the successful drilling of a well. It is used primarily to seal the annulus between the walls of the borehole and the steel casing, to isolate the pressured or weak zones encountered whilst drilling.

The oil-well cement must possess the following properties:

* low permeability
* form a good bond between rock and casing
* maintain these properties under downhole temperature and pressure conditions
* protect the casing against corrosion and collapse

To achieve these aims, the cement slurries must stay pumpable for sufficient time to permit placement, give stable suspensions, harden rapidly once in place and retain high strength and low permeability during well lifetime.

API specification 10 from American Petroleum Institute classifies eight different oil-well cements. Other national standards exist, e.g. in Russia, China, India, most Eastern European countries, but so far no EN standard has been drafted. In Table 3 an overview of API 10 cements is compiled.

Table 3 Overview of oil-well cements

Class	Typical use
A	from surface to 1830 m, special properties not required, ASTM type I
B	from surface to 1830 m, moderate or high sulfate resistance
C	from surface to 1830 m, high early strength
D	between 1830 and 3050 m, moderately high T and p conditions, moderate or high sulfate resistance
E	between 3050 and 4270 m, high T and p conditions, moderate or high sulfate resistance
F	between 3050 and 4880 m, extremely high T and p conditions, moderate or high sulfate resistance
G and H	from surface to 2440 m, for use with accelerators or retarders, moderate or high sulfate resistance, class H coarser than G
J	between 3660 and 4880 m, pure OPC, extremely high T and p conditions

Such cements need special test procedures for suitable characterisation and additional care during manufacture so as to ensure consistency of quality between batches of the same plant.

In use, they are frequently mixed with additives in various proportions to produce satisfactory slurry performance for given well conditions, so they should additionally be compatible and responding to these additives (Table 4).

Table 4 Common types of additives for Oil-well Cements

Classification	Function	Example
Accelerator	Reduces thickening time of cement	$CaCl_2$, sea-water
Retarder	Lengthens thickening time	Lignosulfonates, sugars
Dispersant	Improves flow properties of cement	Superplasticizers
Lightweight extender	Improves stability of suspension	Bentonite, various clays
Weighing agent	Improves density of slurry	Haematite, barite, sand
Lost circulation controller	Prevents cement losses through strata	Walnut shells, cellophane flakes, expanded clay
Inhibitor of strength retrogression	Prevents loss of strength and formation of low strength silicate hydr.	Silica flour, silica sand
Fluid loss controller	Controls rate of water loss	polymers, cellulose
Defoamers	Removes foaming during mixing	Lauryl alcohol, glycols

2.8 White cement

One of the most important special Portland cements. It is characterized by a white colour, obtained with suitable selection of raw materials, in which the colouring elements iron, chromium and manganese must be kept at the lowest possible level. Reduced formation of melt phase during burning is sometimes compensated by addition of fluoride as mineralizer.

Mechanical properties of white cements are comparable to those of OPC. Lower strength binders are produced intergrinding (up to 35%) high purity limestone. To improve whiteness, use of "optical whiteners" such as methylene blue in cement grinding can be applied.

White cement is used for architectural purposes in white or coloured concrete. To achieve best results, a properly coloured aggregate has to be used.

2.9 Hydrophobic cement

A small amount of a water-repellent agent (stearic acid, oleic acid, a.s.o.) is added to Portland cement during grinding. This forms a protective coating around each cement particle that retards hydration until cement is mixed with water and prevents deterioration during storage, especially in humid countries.

2.10 Masonry Cements

Masonry cements are successfully used in the production of mortars and plasters for most non-structural building purposes.

Their main characteristics are: low early- and late strengths, low shrinkage, limited water permeability, high water retention, excellent plasticity and cohesiveness in the fresh state, frequently also air entrainment for better workability and freeze-thaw resistance.

These properties are achieved by a low to medium clinker content, use of a suitable limestone and/or other mineral additions, use of air-entraining agents.

MC's are mostly produced by intergrinding Portland cement clinker, gypsum, precrushed limestone and/or other mineral additions. When the grindability of the constituent materials is much different, it might be opportune to grind them separately, especially if the following blending facilities are available.

The main advantage from the production point of view is the limited clinker content (may be as low as 25%) and the availability of the limestone in the plant. Production

25 Holderbank Group plants produce masonry cements in an extremely wide range of compositions and properties, reported in the following table 5 (based on 1996 Annual Technical Report).

Table 5 **Characteristics of Masonry Cements in the Holderbank Group**

Masonry Cement Characteristics	avg.	min.	max.
Clinker content, % [1)]	54.2	24.0	81.5
Specific surface acc. to Blaine, cm^2/g	6470	3765	9420
Residue on a 45-μm sieve, %	8.9	1.7	25.7
Residue on a 90-μm sieve, %	5.5	1.1	9.5
Air entraining agent, dosage g/t	1210	91	4000
Sulfate content, % SO3	1.93	0.62	3.00
Water demand, % [2)]	26.3	21.5	30.2
Initial setting time, minutes [2)]	190	113	383
Compressive strength 7 days, MPa [2)]	12.8	3.7	25.6
Compressive strength 28 days, MPa [2)]	15.2	3.4	29.5
Specific milling energy consumption, kWh/t	65.6	34.3	132

[1)] main other constituent is limestone, but also fly ash and pozzolana are used

[2)] figures related to both ASTM and EN test methods are considered

2.11 Ultrafine Cements (Microcements)

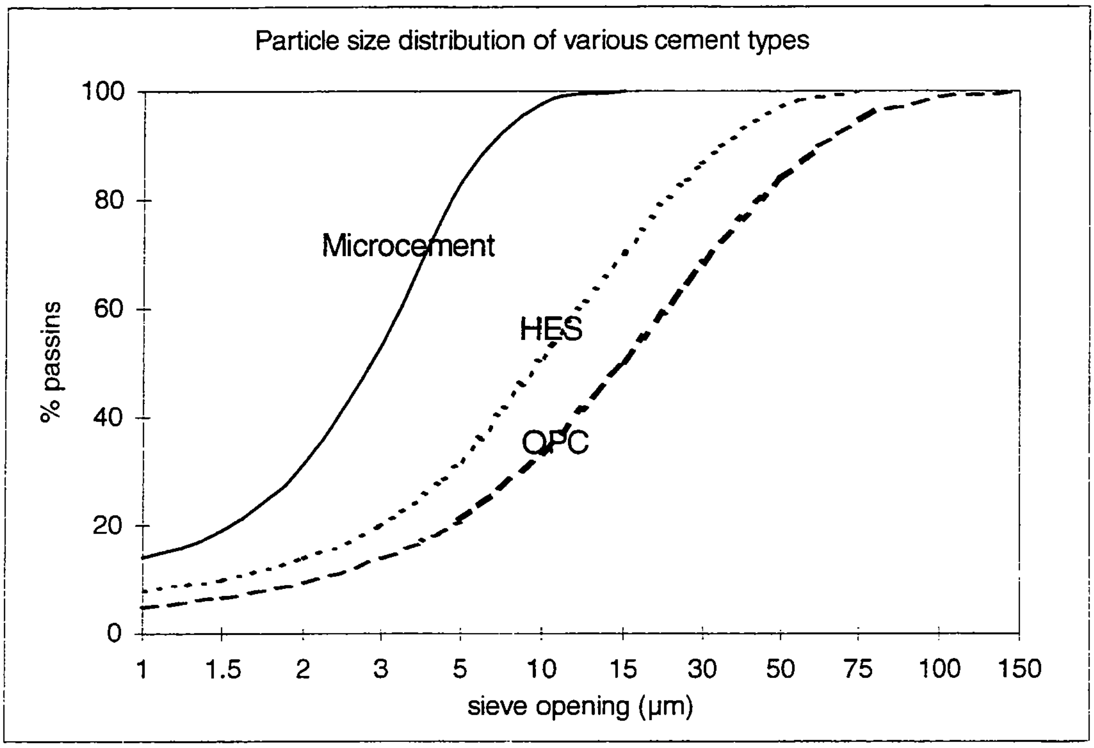
These binders are characterized by a narrow and steep particle size distribution (see figure 1), specially designed for injection grouts used for sealing and improving mechanical properties of porous systems (rocks, damaged concretes, soils).

Due to the reduced particle size, water-microcement suspensions are highly stable and penetrating than OPC grouts. Results obtained using microcement injections are comparable to those of chemical products such as resins and soluble silicates, with the advantage of being more environment friendly.

Microcements are usually Portland or blast furnace slag cement based and are produced by ultrafine grinding or subsequent efficient separation of finer fractions from common cements.

Particle size distribution may range between 0 and 10 -15 μm. Due to this, they also develop much higher early strength than the corresponding common cement , but usually require higher water demand. This is not a drawback in most applications, since for injection grouts a W/C ratio of 1.5 to 3 is quite in the normal range.

Figure 1 **Particle size distribution of various cement types**



As mentioned, their main use is in fields where common cements cannot be used due to their limited fineness characteristics

- agglomeration of loose soils
- sealing of microcracked rocks
- restoration of foundations, tunnels, leaching dams, historical buildings.

2.12 <u>High Alumina Cement</u>

Typical non-Portland cement, high-alumina cement (HAC) produces a concrete which has an exceptionally fast rate of hardening and is resistant to attacks by most sulfate solutions. It also has a higher resistance against acidic solutions than Portland cement based concretes, but it does not resist the attack of caustic alkali.The strength development of HAC is demonstrated in Figure 2. About 80% of its ultimate strength is achieved after only 24 hours. The high rate of strength gain of HAC is due to the rapid hydration of the anhydrous calcium aluminate (CA).

Rapid hardening is not accompanied by fast setting. Initial setting takes place between two and six hours after mixing, becuase of the slow setting pattern of hydration of the main compound CA.

Setting time can be shortened by addition of OPC. HAC/OPC blends are used in applications where rapid setting is compulsory, but lower ultimate strengths are then obtained.

Inversely, the same effect on setting is achieved by replacement of 10 to 20% HAC to OPC.

The high rate of heat evolution (Figure 3) of high-alumina cement (ab. 40 J/g.hour in the first 24 hours) makes it necessary for HAC concrete to be placed in thin sections and never in large mass. The rise in temperature causes cracking and adversely affects strength. HAC concrete needs also more water for hardening and better curing during the first two days than OPC concrete.

The main drawback of high-alumina cement concrete is the loss of strength associated with expansion due to the conversion of the aluminate hydrates under moist conditions at elevated temperatures. The hexagonal hydrate CAH_{10} is converted into the cubic aluminate C_3AH_6 as from the reaction

$$3\ CAH_{10} \rightarrow C_3AH_6 + 2\ AH_3 + 18\ H$$

This means that concrete which is properly placed and has developed a high strength will lose a considerable proportion of its strength upon exposure to temperatures over 30 °C and moisture.

Figure 2 **Strength development of different cements**

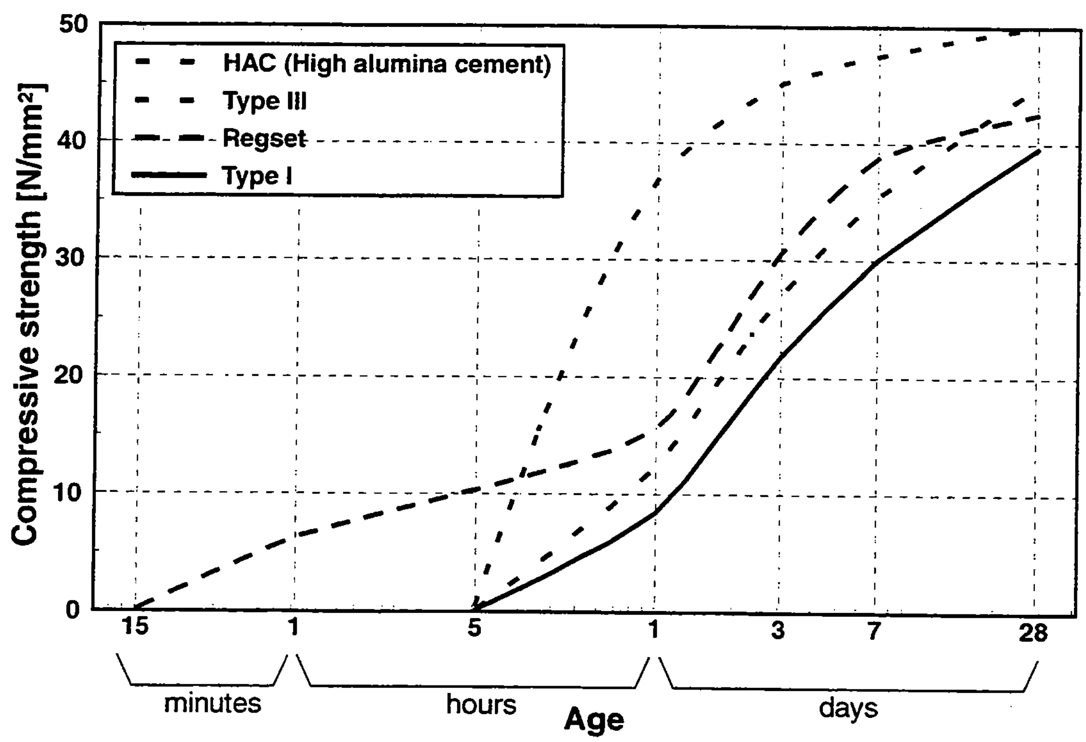
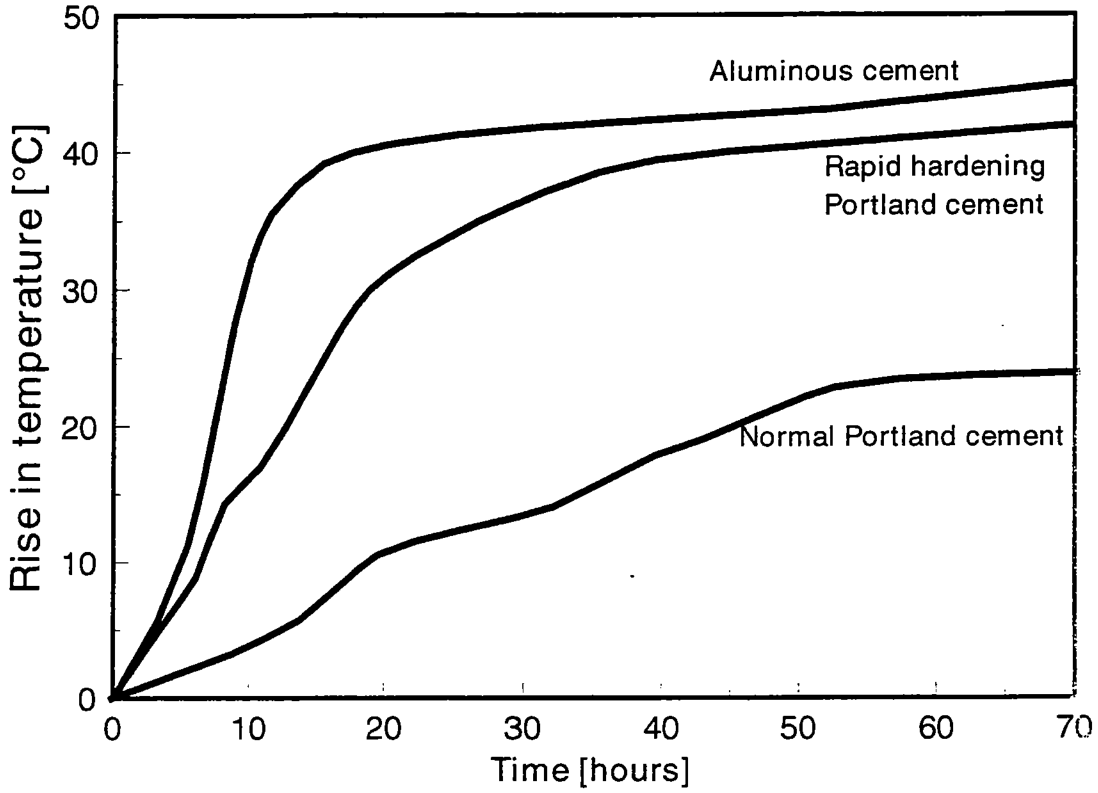


Figure 3 Heat evolution of different cements



2.13 Phosphate cements

A mixture of tetracalcium phosphate and dicalcium phosphate, when mixed with a dilute phosphoric acid or other aqueous solutions will harden like a cement-producing hydroxyapatite, $Ca_{10}(PO_4)_6HOH$, as the final product. The setting property, combined with biocompatibility, makes calcium phosphate cements useful in many applications in dentistry and medicine.

Pastes prepared from diammonium orthophosphate, as well as NaH_2PO_4 or Na-polyphosphate, and calcined MgO exhibit a fast setting and hardening at room temperature associated with NH_3 liberation. MgO-phosphate binders may be used for high temperature applications, since strength remains preserved up to 1000 °C.

2.14 Other non-Portland cements

2.14.1 Alkali-activated cements

"Pyrament " (developed in USA) belongs to this type of binders; they are mainly composed of pozzolans and possibly other active silica-based materials such as silica fume, fly-ash, slag or Portland cement, and alkali compounds (alkali silicate, hydroxide or carbonate); water reducers and retarders are also added to set regulation. They display excellent early strength properties as well as high density and strength at later age, but the complicated multicomponent formulation indicates a very sensitive system, difficult to control under field conditions.

Development of "Geopolymers" is based on the work of Davidovits. The main reaction takes place between sodium hydroxide and kaolinite to form hydrosodalite at room temperatures or preferably between 150 and 180 °C. This reaction is the typical hydrothermal synthesis of zeolites.

2.14.2 Alkali-activated slags

The ability of activating blast furnace slags (BFS) by the addition of alkalis has been known for many decades. Hydration of slag requires the breaking of bonds and dissolution of the three-dimensional structure of glass and this is easily achieved in the high pH environments produced by alkali. Research on slag activation dates back to the early 50's; interest in alkaline activation has grown markedly and in recent years alkali-activated cement and concrete have received greater attention worldwide.

Compared with ordinary Portland cement and interground slag cement, alkali activated slag cement has some advantageous properties, including rapid and high strength development, good durability and high resistance to chemical attack.

Finely ground, well granulated BFS can be utilized in the production of cements suitable for the precast industry, after addition of alkaline activators and superplasticizers, as for the "F" cement (Finland). When used with thermal curing, these cements can develop strengths 30% higher than normal Portland cements.

3. OVERVIEW OF PRODUCTION IMPLICATIONS IN SPECIAL CEMENTS

In the following table 5, the implications related to the production of special cements are summarized. In particular, after highlighting the main properties and applications of each special cement type, a list of special measures that need to be taken at the plant to achieve the expected properties is compiled.

Table 4 Properties , application and measures for proper production of special cements

Type	Properties	Application	Raw mat	Man ufact	Addi tions	App licat ion
OPC	normal workability and stength	general application in building and construction	-	-	-	-
ASTM II / SRC/LHC	moderate sulfate res. low heat of hydration	drainage, large piers and retaining walls, sea water	x	-	(x)	-
ASTM III / HES-RHC	high early strength, rapid hardening	precast concrete, repairs, cold weather concreting	-	x finer	-	-
ASTM IV / LHC	low heat of hydration	mass concrete, large dams	x	-	x	x
ASTM V / SRC	sulfate resistant	severe sulfate action in (soils, ground water)	x	(x)	x	x
Air entrain.	frost resistance	roads, freeze-thaw action	-	-	x	-
Low alkali	low reactivity with amorphous silica	in concrete with reactive aggregates	x	x	x	-
Leaching resisting	low content of hydrat. lime	in presence of pure waters or high CO_2 solutions	x	-	x	-
Oil well	retarded setting, moderate sulfate res.	in oil, gas and other types of wells	x	-	(x)	x
Regset	fast setting time	road repairs, dry mortars	x	x	-	x
White cem	white colour	architectural concrete	x	xx	(x)	x
Sulfoalum. cement	fast setting, high workab., (expansive)	precast concrete, repairs, no-shrinkage concrete	x	x	-	x
Ultrafine	max size < 15 µm	injection grouts	-	xx	(x)	xx
High alum. cement	high early strength, rapid strength devel.	demand of very high early strength, refractories	x	xx	-	xx

4. LITERATURE

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